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NONAQUEOUS ELECTROLESS CHROMIUM PLATING METHOD

U.S. ARMY WEAPONS COMMAND

TECHNICAL REPORT

September 1972

RESEARCH DIRECTORATE
WEAPONS LABORATORY, WECOM
RESEARCH, DEVELOPMENT AND ENGINEERING DIRECTORATE
U. S. ARMY WEAPONS COMMAND

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Under the direction of the Research Directorate of the Weapons Laboratory, WECOM, a nonaqueous chemical method for coating chromium on metal plates was sought. The method involved treatment of chromium salts with a variety of reducing agents. Lithium borohydride in tetrahydrofuran-diethyl ether reduces chromic chloride to the chromous state on mixing, followed by a slower reaction presumed to be the deterioration of chromous borohydride to a "chromium boride" of not well-defined composition. The "boride" forms as a black nonadherent plate preferentially on metal substrates. Trialkylborohydride salts in tetrahydrofuran reduce chromic chloride immediately to colloidal elemental chromium which redissolves if excess chromic chloride is present to form chromous chloride. Dialkylborohydride salts under like conditions produce chromous chloride which is then further reduced to the elemental form. Substitution of either borohydride ion or dimethylborohydride ion with a cyano group resulted in a decrease in the strength of the reducing agent such that chromic chloride could be reduced only to the chromous stage in tetrahydrofuran.

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ABSTRACT

Under the direction of the Research Directorate of the Weapons Laboratory, WECOM, a nonaqueous chemical method for coating chromium on metal plates was sought. The method involved treatment of chromium salts with a variety of reducing agents.

Lithium borohydride in tetrahydrofuran-diethyl ether reduces chromic chloride to the chromous state on mixing, followed by a slower reaction presumed to be the deterioration of chromous borohydride to a "chromium boride" of not well-defined composition. The "boride" forms as a black nonadherent plate preferentially on metal substrates. Trialkylborohydride salts in tetrahydrofuran reduce chromic chloride immediately to colloidal elemental chromium which redissolves if excess chromic chloride is present to form chromous chloride. Dialkylborohydride salts under like conditions produce chromous chloride which is then further reduced to the elemental form. Substitution of either borohydride ion or dimethylborohydride ion with a cyano group resulted in a decrease in the strength of the reducing agent such that chromic chloride could be reduced only to the chromous stage in tetrahydrofuran.

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FOREWORD

This report was prepared by Dr. R. J. Wagner, Advanced Programs, Rocketdyne, Division of North American Rockwell Corporation, under Contract DAAF03-71-C-0283.

The contract was part of a project for the development of a 4.32mm barrel. This program was authorized and funded by the U. S. Army Small Arms System Agency.

The work was conducted under the direction of the Research Directorate, Weapons Laboratory, U. S. Army Weapons Command, with R. H. Wolff as Project Engineer.

OBJECTIVE

The objective of the present work was to conduct chemical studies necessary to define an electroless plating process capable of giving an adherent chromium plate of approximately 1 mil thickness, in terms of bath components, reaction stoichiometry, deposition rate, and throwing power. A further objective, subject to successful plating and preliminary evaluation of several gun barrels, was to define the elements of a circulatory plating device.

INTRODUCTION

From an economic and logistic standpoint, an extension of the useful life of small arms gun barrels is a factor of major importance. Numerous approaches to the solution of this problem have been investigated, including plating of the bore with chromium. The conventional aqueous electroplating process has a number of serious drawbacks, one of which is the exacting fixture requirements for proper electrode positioning to ensure uniform plate thickness.

A non-aqueous electroless process would appear to offer distinct processing advantages in that the plating bath could be simply circulated through the barrel. During pre-contractual work at Rocketdyne, reduction of either chromic or chromous chlorides with lithium borohydride in the presence of a nickel or steel substrate was found to result in a preferential deposition of a black chromium-containing plate on the metal. The solvents for the plating bath were ethers such as tetrahydrofuran, diethyl ether, or diglyme (diethylene glycol dimethyl ether). Addition of aluminum chloride to the bath was found to increase the plating rate. Analysis of the plate, which appeared to be fairly adherent, did not give a complete material balance, but indicated a chromium content in the range of 50 to 75 percent.

EXPERIMENTAL PROCEDURE

Tetrahydrofuran (THF), diethyl ether (DEE), and diglyme (diethyleneglycol dimethyl ether) (DG) were purified by distillation from lithium aluminum hydride. Reagent solutions were prepared from the highest purity materials commercially available and filtered using either vacuum line or dry box techniques before standardization and storage in an inert atmosphere glove box. The following materials were prepared by literature methods; $CrCl_3 \cdot 3THF$ (Refs. 1, 2), $B(CH_3)_3$ (Ref. 3), $[HB(CH_3)_2]_2$ (Ref. 4), and $NaBH(C_2H_5)_3$ (Ref. 5). Adaptations of literature methods were used to prepare $NaBH(CH_3)_3$, $NaBH_2(CH_3)_2$, and $NaBHCN(CH_3)_2$.

The $CrCl_3$ (or $CrCl_2$)-$LiBH_4$-$AlCl_3$ System

The majority of the experiments were performed by mixing known volumes of standardized reagent solutions in screwcap vials containing a nickel coupon. In these experiments, the volume of the plating bath (10.9 ml), the temperature (30°C), and the atmosphere (dry N_2) were held constant while the effects of (1) $CrCl_3$ vs. $CrCl_2$ as the chromium source, (2) concentration of Cr, (3) mole ratio $LiBH_4/CrCl_x$, (4) mole ratio $AlCl_3/LiBH_4$, and (5) volume ratio THF/DEE (tetrahydrofuran/diethyl ether) were varied. The experiments were designed such that statistical treatment of the resulting data could be used to attempt to optimize the process for maximum chromium content of the plate with a minimum number of experiments using a modification of the method of Li (Ref. 6).

The reagent solutions used in the initial series of experiments were the following: 0.044 M $CrCl_3$ in THF (saturated at 30°C); 0.112 M $CrCl_2$ in THF (saturated at 30°C); 0.129 M $AlCl_3$ in DEE; and 0.486 M $LiBH_4$ in DEE. The

order of addition of reagents to the vials was $AlCl_3$, $LiBH_4$, DEE, THF, and $CrCl_3$ (or $CrCl_2$), followed by a nickel coupon of dimensions 1" x 1/4" x 0.002". The coupon had been cleaned by successive washings with trichloroethylene, acetone, distilled water, 4N HCl, and distilled water, followed by vacuum drying at ambient temperature and weighing in air. The experimental quantities are listed in Table I.

A second series of experiments was run using the following reagent solutions: 0.227 M $LiCrCl_3$ and 0.146 M $LiBH_4$ in THF, 0.500 M $LiBH_4$ in DEE, and 0.417 M $AlCl_3$ in DEE. The order of addition of reagents was the same as in the first series. The experimental quantities are listed in Table I.

The duplicate of Experiment 18, which was run under autogenous pressure, was allowed to proceed to completion during 24 hours before 23.3 cc (1.04 mmoles) of non-condensible gas was collected. Hydrolysis of the reaction mixture with 2.0 ml 20% HCl produced an additional 55.6 cc (2.48 mmoles) to account for 93.4% of the hydrogen in the 0.943 mole of $LiBH_4$ used. During the course of the plating, it was observed that the nickel surface and the glass surface which initially had been in contact with the $LiBH_4$ solution plated preferentially.

The Intermediate $Cr(BH_4)_2$

The violet color of a 0.044 M $CrCl_3$ solution in THF was discharged on addition to 0.09 ml of 0.486 M $LiBH_4$ (0.0437 mmole) in DEE until 1.00 ml (0.044 mmole) had been added, indicating the stoichiometry of Equation (1). An attempt to prepare a sufficiently concentrated solution of $CrCl_2$

$$CrCl_3 + LiBH_4 \xrightarrow{THF} CrCl_2 + LiCl + 1/2H_2 + THF{:}BH_3 \qquad (1)$$

Table I

$CrCl_3$ (or $CrCl_2$)-$LiBH_4$-$AlCl_3$-THF-DEE Plating Bath Optimization Experiments

Expt. No.	Reagent Volume, ml[a]						Weight of Ni Coupon, mg.			Plate Wt., mg.
	$AlCl_3$	$LiBH_4$	DEE	THF	$CrCl_3$	$CrCl_2$	Initial	Plated	Stripped	
1	2.96	0.73	5.33	—	1.88	—	71.1	72.6	71.3	1.3
2[b]	2.06	0.96	6.00	0.90	—	0.98	67.4	—	—	—
3	1.98	0.93	6.11	—	1.88	—	64.8	66.4	65.0	1.4
4	5.04	1.24	2.74	0.90	—	0.98	69.7	71.8	69.8	2.0
5	2.96	0.73	3.78	2.69	—	0.74	71.5	73.1	71.3	1.8
6	2.06	0.96	4.45	0.93	2.50	—	68.5	69.1	68.4	0.7
7	2.06	0.96	6.00	0.90	—	0.98	71.5	76.4	71.5	4.9
8	1.98	0.93	4.56	2.69	—	0.74	70.2	70.6	70.0	0.6
9	5.04	1.24	1.19	0.93	2.50	—	68.6	69.6	68.6	1.0
10	0.89	0.93	6.86	0.49	1.73	—	69.8	70.4	69.9	0.5
11	1.36	1.16	6.57	—	1.81	—	66.3	67.5	66.4	1.1
12	1.95	1.40	5.65	—	1.90	—	68.7	70.3	68.5	1.8
17	2.68	1.67	4.56	—	1.99	—	68.7	71.1	68.7	2.4
18	3.55	1.94	3.34	—	2.07	—	69.8	72.0	69.9	2.1
19	4.58	2.24	1.92	—	2.16	—	68.0	69.1	68.3	0.8
20[c]	20.6	17.8	42.6	—	19.0	—	64.8	65.7[d]	65.3	~9[e]
24	1.55	1.08	6.04	1.77	—	0.45[f]	66.9	68.6	67.4	1.2
25	2.38	1.37	5.50	1.18	—	0.47[f]	71.2	73.5	71.7	1.8
26	3.42	1.68	4.79	0.52	—	0.49[f]	68.9	70.6	69.2	1.4
27	4.68	2.01	3.70	—	—	0.51[f]	71.9	72.7	71.5	1.2
28	6.21	2.36	1.79	—	—	0.54[f]	73.6	74.2	73.3	0.9
29	8.02	2.73	—	—	—	0.56[f]	69.3	69.8	69.0	0.8

(a) Experiments 1-19: 0.129 M $AlCl_3$ in DEE, 0.486 M $LiBH_4$ in DEE, 0.044 M $CrCl_3$ in THF, 0.112 M $CrCl_2$ in THF
Experiment 20: 0.204 M $AlCl_3$ in DEE, 0.486 M $LiBH_4$ in DEE, 0.044 M $CrCl_3$ in THF
Experiments 24-29: 0.417 M $AlCl_3$ in DEE, 0.500 M $LiBH_4$ in DEE, 0.227 M $LiCrCl_3$ + 0.146 M $LiBH_4$ in THF

(b) Part of plating solution lost due to foaming; replaced by Experiment 7.

(c) Scaled-up duplicate of Experiment 18 with a bath volume of 100 ml.

(d) Most of plate had flaked off before weighing.

(e) Estimated weight derived by difference between initial Cr and that found in deposit isolated from bath walls.

(f) As its complex salt, $LiCrCl_3$.

so that it would precipitate from solution as a solvate was made by adding 10.0 ml 0.823 M $LiBH_4$ in THF to a slurry of 1.70 g $CrCl_3 \cdot 3THF$ in 10.0 ml THF. The mixture was a clear aqua blue solution, suggesting formation of a complex salt, according to Equation (2). Analysis of this solution was

$$CrCl_3 + LiBH_4 \xrightarrow{THF} LiCrCl_3 + 1/2H_2 + THF{:}BH_3 \qquad (2)$$

made after three months at $30^{\circ}C$, during which time any $THF{:}BH_3$ would decompose by opening of the heterocycle as indicated in Equation (3). The

$$\underbrace{CH_2(CH_2)_3O}{:}BH_3 + 2\underbrace{CH_2(CH_2)_3O} \longrightarrow [CH_3(CH_2)_3O]_3B \qquad (3)$$

concentrations of Cr, Li, B, and hydridic H (0.227 M, 0.373 M, 0.189 M, and 0.560 M, respectively) indicate that most of the BH_3 groups generated (Equation 2) escape from solution as B_2H_6 rather than remaining as a THF adduct.

A reaction mixture consisting of 2.0 ml 0.112 M $CrCl_2$ (0.224 mmole) in THF with 0.92 ml 0.486 M $LiBH_4$ (0.447 mmole) in DEE changed rapidly from pale greenish blue to emerald green and a pale green precipitate formed. The solid contained 80% cf the chromium but gave no hydrogen on dissolution in aqueous HCl. A similar result was obtained when the solvent was diglyme, suggesting that the precipitate was perhaps a hydrated chromium borate.

When the experiment was repeated using a solution prepared from $CrCl_2$ which had been vacuum dried at $150^{\circ}C$ (saturated solution in THF at $30^{\circ}C$ was 0.054 M; c.f., 0.112 M if not dried), a clear green solution was obtained. An attempt to precipitate LiCl from the solution as $LiCl \cdot 2C_4H_8O_2$ by addition of dioxane was unsuccessful.

Solid $CrCl_3$·3THF, when added to 0.500 M $LiBH_4$ in DEE, dissolved and formed a colorless precipitate immediately and, additionally, a black one in a few hours.

The $CrCl_2$–$NaBH(C_2H_5)_3$ System

In preliminary experiments to test the effectiveness of $NaBH(C_2H_5)_3$ as a reducing agent, $CrCl_2$ was used as the source of chromium. In one experiment, a THF solution of $CrCl_2$ was used with excess reducing agent and in the other a THF slurry of $CrCl_2$·xTHF was used with a deficiency of reducing agent.

In the first experiment, the reducing agent (Ref. 5) was prepared from excess $B(C_2H_5)_3$ (v.t. = 12.0 mm at 0°C) and 0.0180 g (0.743 mmole) NaH (assay 99%) and had a mole ratio $B(C_2H_5)_3$/NaH = 1.05. The liquid $NaBH(C_2H_5)_3$ was dissolved in 0.2 ml THF in an evacuated tube containing a nickel coupon and 4.00 ml 0.054 M $CrCl_2$ (0.216 mmole) in THF was introduced. An immediate precipitation of a black colloidal solid and evolution of gas was observed with no evidence of plating on either the coupon or the tube walls. The non-condensible gas (presumably H_2) was 3.85 cc (0.172 mmole).

In the second experiment, 0.0290 g (1.20 mmoles) of 99% NaH, when treated with excess $B(C_2H_5)_3$, produced $NaBH(C_2H_5)_3$ (mole ratio $B(C_2H_5)_3$/NaH = 1.04), which was diluted to 5.00 ml with THF. A 1.00 ml aliquot (0.240 mmole $NaBH(C_2H_5)_3$ was added to 0.0653 g $CrCl_2$·xTHF (0.35 mmole based on Cr analysis of a separate sample which had been vacuum dried under the same conditions) and resulted as before in the immediate formation of a black precipitate which settled in about an hour to reveal a clear blue-green

supernatant liquid. On repeated fractional condensation at -63°C of the volatile portion of the reaction mixture, 0.0075 g (0.076 mmole) of $B(C_2H_5)_3$ was recovered.

To the remaining 4.00 ml of the $NaBH(C_2H_5)_3$ solution (0.96 mmole) was added 1.0 ml of benzene and 4.7 ml 0.054 M $CrCl_2$ (0.254 mmole) in THF. The black precipitate and gassing were observed as before but no evidence for bis (benzene)-chromium was found on attempted high vacuum sublimation of the reaction residue at temperatures up to 230°C.

The $CrCl_3$-$NaBH(C_2H_5)_3$ System

$NaBH(C_2H_5)_3$ (mole ratio $B(C_2H_5)_3/NaH = 0.997$) prepared from 0.0878 g (3.62 mmoles), 99% NaH and excess $B(C_2H_5)_3$ was dissolved in 3.60 ml THF and standardized by hydrolytic analysis of an aliquot (19.64 cc H_2/ml or 0.877 M). A 0.78 (0.684 mmole) quantity of the $NaBH(C_2H_5)_3$ was added dropwise (ca. 0.01 ml drops) from the fine drip tip of a sidearm of the reactor to a magnetically stirred slurry of 0.0859 g (0.229 mmole) of $CrCl_3 \cdot 3THF$ in 3.0 ml of THF at ambient temperature under autogenous pressure. Each drop of reducing agent produced immediate gas evolution and a black precipitate which dissolved rapidly. As the addition progressed, the violet solid $CrCl_3 \cdot 3THF$ dissolved, the violet solution changed to pale green, a colorless solid precipitated, and subsequently became pale green at which point 2.44 cc (0.109 mmole) of non-condensible gas had been produced. Further addition of the reducing agent continued to precipitate the black solid, but it no longer would dissolve in the mixture. On completion of the addition, a further 4.51 cc (0.201 mmole) of non-condensible gas had been generated. Addition of 1.0 ml H_2O to the reaction mixture resulted in separation of the liquid into two phases and rapid formation of 5.33 cc (0.238 mmole) of

non-condensible gas without visible change in the black solid. The entire upper organic phase and approximately two-thirds of the aqueous phase were decanted from the black solid which was thrice washed with THF. The volatiles were distilled from the combined washings and liquid phases, leaving 0.0255 g of a colorless water soluble residue which was found to contain 0.0092 g Na and 0.0152 g Cl (96% NaCl). The black residue, after drying under high vacuum at 80°C, weighed 0.0278 g and dissolved very slowly in 20% H_2SO_4 to give a blue solution found to contain 0.0118 g Cr, 0.0059 g Na, 0.0092 g Cl, and < 0.0001 g B. Water was removed from the volatile portion of the reaction mixture by passage of the vapor through a CaC_2-filled column. Low temperature fractional distillation concentrated the $B(C_2H_5)_3$ in the distillation residue (as shown by infrared spectroscopy) from which it was isolated as an ammonia adduct, 0.0417 g (0.363 mmole) $NH_3:B(C_2H_5)_3$.

The $CrCl_3$-$NaBH(CH_3)_3$ System

Preparation of the trialkylborohydride was effected by treatment of 0.0772 g (3.18 mmoles) of powdered 99% NaH with excess liquid $B(CH_3)_3$ at ambient temperature in a sealed tube for four days. The NaH was placed in the upper end of the slightly inclined tube and maintained slightly cooler than the rest of the tube with a wet cloth wick. Crystals of the slightly soluble product replaced the powdered starting material. The mole ratio $B(CH_3)_3$/NaH = 0.981 was found for the $NaBH(CH_3)_3$ after removing excess $B(CH_3)_3$. The solid was dissolved in 4.0 ml THF and standardized by hydrolytic analysis of an aliquot (15.42 cc H_2/ml or 0.688 M - no CH_4 by mass spectroscopy).

In the same manner and in the same apparatus as was used for the $CrCl_3$-$NaBH(C_2H_5)_3$ reaction, 0.17 ml 0.688 M $NaBH(CH_3)_3$ (0.117 mmole) was added to 0.0416 g (0.116 mmole) $CrCl_3 \cdot 3THF$. No differences between the methyl- and ethyl-substituted reducing agents were observed. At this point, 1.46 cc (0.065 mmole) of non-condensible gas had been generated. Another 0.34 ml 0.688 M $NaBH(CH_3)_3$ (0.234 mmole) was added to the reactor sidearm and upon completion of the reduction, an additional 2.12 cc (0.095 mmole) of non-condensible gas was obtained. An attempt to recover $B(CH_3)_3$ from the volatile portion of the reaction mixture was unsuccessful because of weak complexing with the basic THF. The 0.0294 g of residual black solids on treatment with 0.5 ml H_2O generated 2.26 cc (0.101 mmole) of non-condensible gas. After removal of the water, the residual 0.0300 g of solid was dissolved in 1.0 ml 6N H_2SO_4 and was found to contain 0.0059 g Cr, 0.0091 g Na, 0.0124 g Cl, and 0.0003 g B.

The $CrCl_3$-$NaBH_2(CH_3)_2$ System

A mixture of 200.8 cc (8.96 mmoles) $B(CH_3)_3$ and 51.0 cc (2.28 mmoles) B_2H_6 was allowed to stand in a 200 cc bulb at ambient temperature for four days before $[(CH_3)_2BH]_2$ was isolated by fractional condensation at -78°C. The weight of $[(CH_3)_2BH]_2$ was determined to be 0.2518 g (3.01 mmoles) by difference between that of the original reagents and that of the other more volatile methyldiboranes. The $[(CH_3)_2BH]_2$ was condensed at -196°C onto a slurry of 0.2137 g, (8.81 mmoles) of powdered 99% NaH in 1.0 ml THF in one arm of a Schlenk tube. As the tube warmed, a crystalline product formed and the liquid became quite viscous as the temperature rose to about 40°C. An additional 3.0 ml of THF was added and the resulting solution was

filtered through a medium glass frit into the other arm of the tube. An aliquot of the filtrate was standardized by hydrolytic analysis (64.4 cc H_2/ml or 1.44 M; 0.0325 g Na/ml or 1.41 M).

A 0.85 ml quantity of the 1.44 M $NaBH_2(CH_3)_2$ solution (1.23 mmoles) was added dropwise from the reactor sidearm to a slurry of 0.1537 g (0.410 mmole) $CrCl_3 \cdot 3THF$ in 1.0 ml THF. The violet color of the solution was immediately changed to a pale green in the vicinity of the added reducing solution and a colorless precipitate was observed. When the last of the violet $CrCl_3 \cdot 3THF$ had dissolved, the colorless solid became pale green and 4.68 cc (0.209 mmole) of non-condensible gas was found. Continued addition of the reducing solution resulted after about one minute in the development in the slurry of a uniform gray color. After completion of the addition of the reducing agent, an additional 13.1 cc (0.586 mmole) of non-condensible gas had been generated and a total of 17.9 cc (0.80 mmole) had formed after two days. After removal of the volatiles, treatment of the residue with 0.3 ml H_2O produced 15.9 cc (0.710 mmole) of non-condensible gas. The black solid remaining was dissolved on addition of 1.0 ml 6N H_2SO_4 with formation of 5.62 cc (0.251 mmole) of non-condensible gas. Analysis of the hydrolyzate showed 0.0217 g Cr, 0.0306 g Na, 0.0390 g Cl, and 0.0031 g B.

The $CrCl_3$-$LiBH_4$-Olefin System

Under an inert atmosphere, 10.0 ml 0.044 M $CrCl_3$ in THF (0.44 mmole) was added to each of two tubes containing a chrome-moly-vanadium steel coupon, 3.0 ml 0.486 M $LiBH_4$ (1.46 mmoles) in THF, 1.0 ml 2-methyl-2-butene (9.4 mmoles), and 0.10 ml 0.204 M $AlCl_3$ in DEE (one tube only). A color change from violet to emerald green was accompanied by gas evolution which decreased in amount over seven hours. After standing overnight, a black

precipitate had formed and settled without evidence of plating the metal coupon or the tube walls. As more black solid formed over a five-day period, the color of the solution gradually changed from green to brown and a very thin black plate formed on both metal and glass surfaces. Mechanical losses of the precipitates were substantial on isolation by filtration. The isolated solid from one experiment weighed 0.0153 g and analyzed 52.2% Cr and 14.8% B (B/Cr = 1.37) after dissolution in 20% HCl. The solid from the other experiment (in which $AlCl_3$ was used) weighed 0.0213 g and was insoluble (after vigorous momentary gas evolution) in either 68% HNO_3 or in 10% HNO_3. On subsequent dissolution in 20% HCl, it was analyzed as 25.7% Cr and 5.1% B (B/Cr = 0.95).

Another experiment was conducted under vacuum conditions so that evolved hydrogen might be measured. A 1.0 ml aliquot of a chromous solution (prepared by reaction of 10.0 ml 0.823 M $LiBH_4$ (8.23 mmoles) in THF with 1.70 g $CrCl_3 \cdot 3THF$ (4.54 mmoles) in 10.0 ml THF) was added to 0.90 ml 0.486 M $LiBH_4$ in DEE to give a solution containing $LiCrCl_3$ (0.227 mmole), $LiBH_4$ (0.583 mmole), and $THF \cdot BH_3$ (0.043 mmole). After addition of 0.44 ml (4.1 mmoles) of 2-methyl-2-butene to this pale blue solution, the color became a more intense blue during 15 minutes, a black precipitate was observed to form overnight, and the solution had become colorless in another 24 hours. A 12.20 cc (0.545 mmole) quantity of noncondensible gas had been produced. The 0.0165 g of black solid was isolated by centrifugation and dissolved in 20% HCl as was the residue from the liquid portion of the reaction mixtrue. Analysis indicated the solid to contain 0.0104 g Cr (0.200 mmole) and 0.0032 g B (0.30 mmole), while only 0.0007 g Cr remained in the solution.

The $CrCl_3$-$NaBH_3CN$ System

A 25 g quantity of commercial $NaBH_3CN$, in which the major impurities are borates, was purified (Ref. 7) by dissolution in 125 ml of THF and reprecipitation on adding the THF solution to 450 ml of dry CH_2Cl_2. A solution of 2.5 g of purified $NaBH_3CN$ in 100 ml THF was standardized by hydrolytic analysis of a 2.0 ml aliquot (25.8 cc H_2/ml, 0.0184 g Na/ml; 0.0084 g B/ml; Na/B/H = 1.03/1/2.96).

In the first of two exploratory experiments, 1.00 ml 0.383 M $NaBH_3CN$ (0.383 mmole) in THF was added to 1.75 ml 0.044 M. $CrCl_3$ (0.077 mmole) in THF in the presence of a nickel coupon. The violet color of the solution changed on mixing to emerald green without evidence of gas evolution. (In a separate test, 0.038 mmole $NaBH_3CN$ required addition of 0.039 mmole $CrCl_3$ before the violet color of Cr(III) persisted in the THF solution.) Within two to three hours, a colorless precipitate had deposited from the now gray-green solution. On standing overnight, the solution color had become rose and has remained without further visible change of any kind.

The second experiment was a duplicate of the first, except that 0.50 ml 0.204 M. $AlCl_3$ in DEE was mixed with the $CrCl_3$ before addition of the $NaBH_3CN$. A turbidity was noted on addition of the reducing agent, but no gassing or change in color of the violet $CrCl_3$ was observed other than the decreased intensity due to dilution. During three to four hours, a colorless precipitate settled from the now pale pink solution. On standing overnight, the mixture acquired a gray cast without evidence of plating and has remained without further change.

The $CrCl_3$-$NaBHCN(CH_3)_2$ System

A 1.90 ml quantity of a THF solution of 1.44 M $NaBH_2(CH_3)_2$ (2.74 mmoles) was treated with 61.6 cc (2.75 mmoles) HCN to obtain 61.7 cc (2.75 mmoles) of non-condensible gas. The $NaBHCN(CH_3)_2$ solution was standardized by hydrolysis of a 0.50 ml aliquot (40.0 cc H_2/ml; 0.0396 g Na/ml). The analytical data indicates that the stoppered analyzed 1.44 M $NaBH_2(CH_3)_2$ solution had concentrated by evaporation of solvent to approximately 1.78 M so that 3.38 mmoles had been used. Thus, the HCN treated THF solution was a mixture of approximately 1.45 M $NaBHCN(CH_3)_2$ and 0.17 M $NaBH_2(CH_3)_2$.

A 0.48 ml quantity of the 1.45 M $NaBHCN(CH_3)_2$ (0.696 mmole) and 0.17 M $NaBH_2(CH_3)_2$ (0.082 mmole) THF solution was added dropwise from the sidearm of the reactor to a slurry of 0.1061 g (0.283 mmole) $CrCl_3 \cdot 3THF$ in 0.50 ml THF at ambient temperature under autogenous pressure. With addition of each drop of the reducing solution, gassing and change of the violet color to pale green was observed in the solution. When all of the $CrCl_3 \cdot 3THF$ had dissolved, the mixture had become a turbid gray and 0.812 cc (0.036 mmole) of non-condensible gas had been produced. The mixture appeared unchanged upon completion of the addition of reducing solution which resulted in formation of an additional 1.32 cc (0.059 mmole) of non-condensible gas. On standing overnight, a light gray precipitate had settled, leaving a clear aqua-blue solution.

To the sidearm was added 0.82 ml 0.688 M $NaBH(CH_3)_3$ (0.564 mmole) which was then added dropwise to the blue solution. Immediate gassing and formation of a black precipitate was observed. An additional 4.77 cc (0.213 mmole) of non-condensible gas was produced. The volatile portion of the mixture was removed at ambient temperature and the residue was treated with 1.0 ml H_2O, which resulted in formation of 6.6 cc (0.292 mmole) of non-condensible gas.

RESULTS AND DISCUSSION

The $CrCl_3$ (or $CrCl_2$)-$LiBH_4$-$AlCl_3$ System

Selection of this plating bath system was made on the basis of precontractual work at Rocketdyne in which it was shown that a black chromium-containing plate was deposited on either nickel or steel coupons. In order to optimize the chromium content of the plated deposit with a minimum of experiments, the experiments were designed so that the data obtained could be treated statistically by a modification of the method of Li (Ref. 6) as summarized on the worksheet (Figure 1). The variables to be studied were (A) concentration of chromium (mmoles/liter), (B) $LiBH_4/CrCl_x$ (x=2 or 3) mole ratio, (C) $AlCl_3/LiBH_4$ mole ratio, (D) THF/DEE volume ratio, and (e) the initial valence of the chromium chloride, either Cr(III) or Cr(II). The experimental parameters (Figure 1, lines 7-14 and columns A-E) used in the series of eight tests resulted in the data shown in column H (percent Cr in plated deposit).

Analysis of the data consists of a series of simple arithmetical operations: first, column J is filled in by the sums of consecutive pairs of data from column H, followed by the differences of the same data pairs in which the first number in the pair is subtracted from the second; second, the procedure is repeated twice, using consecutive pairs from column J to fill in column K and those from K to obtain L; third, the effects of the variables studied are obtained by dividing the numbers in column L by the number of experiments. The average (line 7, column M) is the result which would have been expected had an experiment been done with all variables at their base levels. The effects (column N) are interpreted as a measure of the change in chromium content of the plate caused by a unit (as defined on line 4) increase in the associated variables. Discontinuous variables are arbitrarily assigned

Line	Factors Studied		A	B	C	D	E	F	G	Interactions					
2			Cr mM/1	$LiBH_4$/$CrCl_3$	$AlCl_3$/$LiBH_4$	THF/DEE	Cr^{+++} or Cr^{++}			C = AB					
3	Base Level		8.84	4.86	0.825	0.333				E = AD					
4	Unit		1.26	0.62	0.255	0.125				F = BD G = ABD					
5	High Level		10.10	5.48	1.08	0.458	Cr^{+++}			H	J	K	L	M	N
6	Low Level		7.58	4.24	0.570	0.208	Cr^{++}			Data	Calculation			Effects of Factors	
7	Sample 1	Test	7.59	4.29	1.08	0.208	Cr^{+++}			49	54.1	146.1	262.9	32.9	Average
8	2		10.1	4.25	0.570	0.208	Cr^{++}			5.1	92.0	116.8	17.3	A	2.2
9	3		7.59	5.47	0.564	0.208	Cr^{+++}			46	34.8	-43.9	85.1	B	10.6
10	4		10.1	5.47	1.08	0.208	Cr^{++}			46	82.0	61.2	46.7	C	5.8
11	5		7.60	4.28	1.08	0.458	Cr^{++}			2.8	-43.9	37.9	-29.3	D	-3.7
12	6		10.1	4.25	0.570	0.458	Cr^{+++}			32	0.0	47.2	105.1	E	13.1
13	7		7.60	5.45	0.564	0.458	Cr^{++}			25	29.2	43.9	9.3	F	1.2
14	8		10.1	5.47	1.08	0.458	Cr^{+++}			57	32.0	2.8	-41.1	G	-5.1
15	Effect		2.2	10.6	5.8	-3.7	13.1								
16	Effect x Unit		2.77	6.57	1.48	-0.46									
17	Change (1/6)		0.46	1.10	0.247	-0.077	Cr^{+++}								
18	Best Path 24		9.30	5.96	1.072	0.256	Cr^{+++}			85					
19	25		9.76	7.06	1.319	0.179	Cr^{+++}			63					
20	26		10.22	8.16	1.566	0.102	Cr^{+++}			66					
21	27		10.68	9.26	1.813	(0.049)	Cr^{+++}			72					
22	28		11.14	10.36	2.060	(0.052)	Cr^{+++}			78					
23	29		11.60	11.46	2.307	(0.052)	Cr^{+++}			68					
24															
25															
26															
27															

(NOTE: Parenthetical values in Column D represent experimental values in excess of those indicated by the incremental change due to physical limitations, i.e., concentration of reagent solution used.)

Figure 1 NONAQUEOUS ELECTROLESS CHROMIUM PLATING WORKSHEET

with positive effects indicating the high level. The percentage of chromium in the plate would be increased on (1) increasing the concentration of chromium in the bath, (2) increasing the $LiBH_4/CrCl_x$ mole ratio, (3) increasing the $AlCl_3/LiBH_4$ mole ratio, (4) decreasing the THF/DEE volume ratio, and (5) using $CrCl_3$ rather than $CrCl_2$ as the source of chromium.*

To determine the most direct path to follow to maximize the chromium content of the plate, the values in column N are transferred to line 15, multiplied by the corresponding unit (from line 4), and entered on line 16. These values are the relative amounts that each variable should be changed to follow the "best path" vector. The actual changes to be made are determined by multiplication of each of the values by a constant to preclude numerical values which would exceed the physical limits of the system without completion of sufficient experiments to indicate trends.

As a result of an experimental error, the amount of $AlCl_3$ in the first eight experiments was far in excess of the predetermined amount. This error, although fortuitous since the data obtained indicated a still higher concentration of $AlCl_3$ would be beneficial, went undetected until after the subsequent series of six optimization experiments had been completed. The same error was not made in the latter experiments and, as a result, low concentrations of $AlCl_3$ based on small increases from the original predetermined values were used - values far too low to provide a valid assessment of the effects of the variables on the chromium content of the

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*Since the $CrCl_3$ is reduced to $CrCl_2$ on mixing with the reducing agent, the initial valence state should not influence the percentage of chromium in the plate. It was subsequently shown that the $CrCl_2$ used to prepare the reagent solution was not completely anhydrous, thus making it inferior to the $CrCl_2$ prepared by <u>in situ</u> reduction of anhydrous $CrCl_3 \cdot 3THF$.

plate. Accordingly, a second series of six optimization experiments (24 to 29) was run. In these experiments, as in the previous series, the required decrease in THF content of the bath could not be attained using the saturated solution of $CrCl_3$ in THF. Consequently, the chromium reagent solution was prepared from solid $CrCl_3 \cdot 3THF$ and an excess of $LiBH_4$ in THF which reduced it to $CrCl_2$ in the form of its highly soluble complex salt $LiCrCl_3$. Even with this modification, the indicated THF/DEE ratio was exceeded in some experiments.

In both the first and second series of optimization experiments, an increase in the chromium content of the plate was found with higher values for the second series as expected. In both series, a significant amount of boron was co-deposited. The variation in the B/Cr mole ratio suggests that no definite chromium boride was formed preferentially. It may be speculated that by loss of hydrogen and/or borane groups from chromous borohydride, a polymeric structure results, which is comprised of Cr-B, B-B, and B-H bonds in varying proportion.

The composition of the black deposit was further investigated by scaling-up one of the experiments (No. 18) approximately nine-fold while maintaining the area of the basis metal coupon the same to obtain a thicker plate (Experiment 20). The larger run showed an increased induction period (Table II), but was otherwise the same. The deposition on the bath walls began five hours after that on the metal and was observed to blister 52 hours after preparation of the bath. An estimated 95% of the deposit on the coupon spontaneously flaked off on evaporation of the solvent. The thickness of the plate was estimated to be 0.2 mil from the weight, an assumed density of 5.0, and the analysis of the isolated deposit. Dissolution of the X-ray amorphous powder in 20% HCl resulted in evolution of hydrogen and boranes (detected by their characteristic odor). The ratio

Table II

Plate Composition from the $CrCl_3$(or $CrCl_2$)-$LiBH_4$-$AlCl_3$ System in Tetrahydrofuran-Diethyl Ether

Expt. No.	Initial Mole Ratio[a]			Induction Period, Hrs	0.5 in^2 Plate					
	Cr	B	Al		Wt, mg	Cr, mg	B, mg	% Initial Cr	B/Cr	Cr + B, %
1	1	4.29	4.62	< 16	1.3	0.64	0.39	15	2.9	79
7	(1)	4.25	2.42	96 < 160	4.9	0.25	0.39	4.4	7.5	13
3	1	5.47	3.08	18	1.4	0.64	0.40	15	3.0	74
4	(1)	5.47	5.91	24 < 40	2.0	0.92	0.60	16	3.1	76
5	(1)	4.28	4.61	168 < 256	1.8	0.048	0.00	1.1	0	3
6	1	4.25	2.42	72 < 88	0.7	0.19	0.00	3.3	0	27
8	(1)	5.45	3.08	216 < 232	0.6	0.15	0.033	3.5	1.1	30
9	1	5.47	5.91	< 15	1.0	0.57	0.36	9.9	3.0	93
10	1	5.94	1.51	26	0.5	0.13	0.020	3.3	0.74	30
11	1	7.09	2.20	6 < 21	1.1	0.56	0.033	14	2.8	81
12	1	8.13	3.01	< 4	1.8	0.90	0.55	21	2.9	81
17	1	9.27	3.95	3	2.4	1.44	0.59	32	2.0	85
18	1	10.35	5.03	1.5 < 3	2.1	1.39	0.57	29	2.0	93
19	1	11.46	6.22	8 < 72	0.8	0.33	0.32	6.7	0.97	81
20	1	10.35	5.03	24	~9[b]	26.1[c]	11.0[c]	11	2.06	77
24	1	5.94	6.33	6.0	1.2	1.02	0.30	19	1.4	110
25	1	7.03	9.27	3.5	1.8	1.14	0.33	21	1.4	82
26	1	8.22	12.85	2.5	1.4	0.93	0.29	16	1.5	87
27	1	9.30	16.83	0.4	1.2	0.86	0.24	14	1.4	92
28	1	10.24	21.06	0.4	0.9	0.70	0.24	11	1.6	104
29	1	11.39	26.33	0.4	0.8	0.54	0.15	8.1	1.3	86

(a) Parenthetical values indicate $CrCl_2$ as starting material.

(b) By difference between initial Cr and that found in isolated deposit.

(c) From analysis of 48.1 mg of deposit from container walls.

$Cr/B/H_2$ = 1/2.06/6.82 is consistent with the proposed structure comprised of Cr-B, B-B, and B-H bonds, each of which would produce hydrogen on acid hydrolysis.

A duplicate of Experiment 18, run under autogenous pressure, indicated over 55% of the hydrogen atoms in the $LiBH_4$ were converted to hydrogen gas in 24 hours. The mole ratio H_2/Cr = 11.4 indicates catalytic decomposition of $LiBH_4$, although the boron which should have been formed was not found in the black deposit of Experiment 18. During the course of the plating, both the metal coupon and the glass surface which had initially been in contact with the $LiBH_4$ solution plated preferentially, suggesting adsorbed BH_4^- ions may be responsible for the surface reactivity.

The Intermediate $Cr(BH_4)_2$

A plausible intermediate in the formation of the black plate from either $CrCl_3$ or $CrCl_2$ on reduction with $LiBH_4$ is the unreported chromous borohydride, $Cr(BH_4)_2$. In an unsuccessful attempt to isolate this compound from THF solution, it was established that $CrCl_2$, formed by reduction of $CrCl_3$ with an equimolar quantity of $LiBH_4$, remained in solution as a complex salt, $LiCrCl_3$, while a major amount of the by-product borane groups escaped as diborane. Also noted in the course of these experiments was the

$$CrCl_3 + LiBH_4 \longrightarrow LiCrCl_3 + 1/2H_2 + THF{:}BH_3 \qquad (4)$$

$$2THF{:}BH_3 \rightleftharpoons 2THF + B_2H_6 \qquad (5)$$

partial hydration of the commercial $CrCl_2$ which enhanced its solubility in THF and interferred with formation of the black plate during reduction with $LiBH_4$.

In THF, a mixture of $CrCl_2$ and $LiBH_4$ formed a green solution which was stable for months, while the same components in DEE deposited both white and black precipitates in a few hours, suggesting perhaps that $Cr(BH_4)_2$ is an unstable intermediate in the formation of "CrB_2" in the THF-DEE solvent system.

The $CrCl_2$–$NaBH(C_2H_5)_3$ System

The trialkyl-substituted borohydrides were evaluated as reducing agents for chromium chlorides since in theory the boron should be released on reaction as triethylborane which would not interact further with the chromium and hence provide a boron-free deposit. With $CrCl_2$ and $NaBH(C_2H_5)_3$, the reaction would presumably occur according to Equation (6).

$$CrCl_2 + 2NaBH(C_2H_5)_3 \xrightarrow{THF} Cr + H_2 + 2NaCl + 2B(C_2H_5)_3 \qquad (6)$$

In a preliminary experiment using a 1.73-fold excess of reducing agent, 80% of the theoretical hydrogen was obtained in an immediate reaction which precipitated a brownish-black solid, only part of which settled. In a second experiment, using a 2.9-fold excess of $CrCl_2$, immediate gassing and formation of the black precipitate were observed and 32% of the theoretical triethylborane was isolated from the reaction mixture. In this second experiment only, the seemingly colloidal precipitate was unstable and settled completely in a few hours. A third experiment using a 1.89-fold excess of reducing agent was conducted in the presence of a large excess of benzene to determine if bis(benzene)chromium could be prepared and thus establish that the black precipitate was elemental chromium. No evidence for this organochromium compound was found.

The $CrCl_3$-$NaBH(C_2H_5)_3$ Systems

Substitution of the well characterized solid, $CrCl_3 \cdot 3THF$, for the THF solution of $CrCl_2$ as the source of chromium was made to attempt to define the stoichiometry of the rapid reaction with $NaBH(C_2H_5)_3$ and establish that pure chromium was precipitated. Such information would be necessary for establishing conditions required to control the rate of chromium deposition. As with the $CrCl_2$, each drop of $NaBH(C_2H_5)_3$ solution added to the $CrCl_3$ solution resulted in immediate gas evolution and formation of a black precipitate which in this reaction dissolved rapidly in the reaction mixture. These observations are consistent with the reactions indicated by Equations (7) and (8).

$$CrCl_3 + 3NaBH(C_2H_5)_3 \longrightarrow Cr + 3/2H_2 + 3NaCl + 3B(C_2H_5)_3 \qquad (7)$$

$$Cr + 2CrCl_3 \longrightarrow 3CrCl_2 \qquad (8)$$

As the addition of reducing agent progressed, the $CrCl_3 \cdot 3THF$ dissolved and was replaced by a colorless solid which changed to pale green when 95% of the hydrogen indicated by Equation (9) had been evolved.

$$CrCl_3 + NaBH(C_2H_5)_3 \longrightarrow CrCl_2 + 1/2H_2 + NaCl + B(C_2H_5)_3 \qquad (9)$$

Further addition of reducing agent resulted in an increasing quantity of the black precipitate which remained undissolved. When the stoichiometry of Equation (7) was reached, 88% of the theoretical hydrogen had been released. Addition of water to the mixture generated much more hydrogen than could be formed by hydrolysis of the remaining B-H bonds. This observation is consistent only with the reaction of finely divided elemental chromium with water.

$$Cr + H_2O \longrightarrow CrO + H_2 \qquad (10)$$

Material balances found on analysis were: (1) black precipitate, Cr = 100%; (2) water soluble, Na = 96%, Cl = 100%; (3) volatile portion of mixture, B = 53% isolated as $NH_3:B(C_2H_5)_3$ which is somewhat more readily separated from THF than $B(C_2H_5)_3$ itself.

The $CrCl_3$-$NaBH(CH_3)_3$ System

The previously uncharacterized salt, $NaBH(CH_3)_3$, was selected as a candidate reducing agent for $CrCl_3$ for two reasons: (1) it would presumably verify the result obtained with the corresponding triethyl homolog, and (2) it would be more closely related to other novel candidate reducing agents, the dialkyl-substituted borohydrides, of which $NaBH_2(CH_3)_2$ should be more readily prepared in a pure state than $NaBH_2(C_2H_5)_2$.

The solid salt, $NaBH(CH_3)_3$, was prepared by interaction of powdered NaH with liquid $B(CH_3)_3$ at ambient temperature and characterized both synthetically and analytically. Its reaction with $CrCl_3$ in THF produced an immediate precipitation of elemental chromium and paralleled that of the ethyl homolog, i.e., 112% of the theoretical hydrogen expected from the reduction of Cr(III) to Cr(II) (Equation 9), 92% of that expected for reduction to Cr(0) (Equation 7), and 87% of the theoretical on reaction with water (Equation 10).

The $CrCl_3$-$NaBH_2(CH_3)_2$ System

The candidate reducing agent, $NaBH_2(CH_3)_2$, could be expected on theoretical grounds to reduce chromium salts at a rate intermediate between that of the BH_4^- ion (slow) and the $BH(CH_3)_3^-$ ion (rapid). Steric, as well as electronic considerations, would indicate little likelihood of Cr-B bond formation so that the reduction of chromium salts should yield boron-free chromium. A synthesis for $NaBH_2(CH_3)_2$, however, has not been reported in the literature.

The preparative route used for $NaBH(CH_3)_3$, namely interaction of the triborane derivative with NaH at ambient temperature, could not be used because of the facile disproportionation under these conditions of the required intermediate, tetramethyldiborane. Accordingly, the synthesis was modified by conducting the reaction with excess NaH at initially low temperatures in THF which should stabilize the borane as its adduct, $THF \cdot BH(CH_3)_2$, and solvate the soluble product, $NaBH_2(CH_3)_2$, formed according to Equation (11).

$$[BH(CH_3)_2]_2 + 2NaH \xrightarrow{THF} 2NaBH_2(CH_3)_2 \qquad (11)$$

Analysis of the resulting THF solution indicated a mole ratio of H/Na = 2.04 in the product.

Reduction of $CrCl_3 \cdot 3THF$ by dropwise addition of a THF solution of $NaBH_2(CH_3)_2$, followed the stoichiometry of Equation (12) without formation and dissolution of elemental chromium (102% of theoretical H_2 evolved). Further reduction resulted in formation of a gray precipitate (presumably

$$CrCl_3 + NaBH_2(CH_3)_2 \xrightarrow{THF} CrCl_2 + NaCl + 1/2H_2 + THF \cdot BH(CH_3)_2 \qquad (12)$$

elemental chromium) in about a minute but on completion of the addition of reducing agent, 143% of the theoretical hydrogen expected, according to Equation (13), had been produced. Additional hydrogen generated after standing for two days at ambient temperature brought the total to 195% of that expected.

$$CrCl_2 + 2NaBH_2(CH_3)_2 \xrightarrow{THF} Cr + H_2 + 2NaCl + 2THF \cdot BH(CH_3)_2 \qquad (13)$$

Since it appears that all of the hydride had been oxidized to elemental hydrogen, it is suggested (Equation 14) that the boron moiety is reduced to $(CH_3)_2BB(CH_3)_2$, a reportedly (Ref. 8) unstable species which might be stabilized in THF or perhaps disproportionate to $B(CH_3)_3$ and $(BCH_3)_x$ (Equation 15).

$$CrCl_2 + 2NaBH_2(CH_3)_2 \longrightarrow Cr + 2H_2 + 2NaCl + (CH_3)_2BB(CH_3)_2 \qquad (14)$$

$$(CH_3)_2BB(CH_3)_2 \longrightarrow B(CH_3)_3 + (BCH_3)_x \qquad (15)$$

On treatment with water, the chromium would be expected, on the basis of Equation (10), to generate an equimolar amount of hydrogen. The quantity of hydrogen produced was 86.6% of that expected when combined with that from hydrolysis of residual B-H bonds.

$$THF \cdot BH(CH_3)_2 + 1/2H_2O \longrightarrow (CH_3)_2BOH + THF + H_2 \qquad (16)$$

On acidification of the mixture, more hydrogen was formed than could be accounted for by the reactions of Equations (10) and (16), but reduction of water by chromous ion in acid solution is expected. On the basis of Equations (10) and (17), 93.2% of the theoretical hydrogen was found.

$$Cr^{++} + H_3O^+ \longrightarrow Cr^{+++} + H_2O + 1/2H_2 \qquad (17)$$

Thus, it appears that elemental chromium is precipitated from $CrCl_3$ solution in THF when $NaBH_2(CH_3)_2$ is the reducing agent and although the reaction is somewhat slower than when $NaBH(CH_3)_3$ is used, the deposition is too rapid for application in a plating bath system.

The $CrCl_3$-$LiBH_4$-Olefin System

This system was considered for the potential *in situ* generation of alkyl-substituted borohydrides on the one hand, and for potential prevention of boron incorporation in the chromium deposit on the other. The olefin, 2-methyl-2-butene, was selected because its addition to a BH_3 group is limited by steric considerations of two of the three B-H bonds. Thus, reactions such as are indicated in Equations (18) and (19) might reasonably be expected to occur.

$$CrCl_3 + 3LiBH_4 + 6(CH_3)_2C{=}CHCH_3 \xrightarrow{THF} Cr + 3/2H_2 + 3LiCl + 3[(CH_3)_2CH(CH_3)CH]_2BH \qquad (18)$$

$$[(CH_3)_2CH(CH_3)CH]_2BH + LiBH_4 \xrightarrow{THF} LiBH_2[CH(CH_3)CH(CH_3)_2]_2 + BH_3 \qquad (19)$$

The black deposits formed in this system, however, contained significant amounts of boron, i.e., $0.95 < B/Cr < 1.37$. The deposits, although of lesser boron content, were quite similar to those formed in comparable times in the absence of the olefin. Similarly, the amount of hydrogen generated was in excess of the 1.5 moles/mole Cr just as it was in the absence of olefin. Under the reaction conditions used, the olefin was competing with chromium for boron but was not successful in preventing incorporation of boron in the deposited plate.

The $CrCl_3$-$NaBH_3CN$ System

Because of the electron withdrawing power of the cyano group, reductions with the cyanoborohydride ion are much slower than with borohydride ion (Ref. 9). The slower rate, when coupled with the known ability to reduce certain transition metal ions to the elements (Ref. 10), made this substituted borohydride ion worthy of study with chromium salts. The potential stabilizing effect of cyano group in making reduction of chromium salts more difficult was recognized at the outset and from the experimental results appears dominant. Mixing of $CrCl_3$ and $NaBH_3CN$ in THF solution resulted in color changes that may be due to either reduction of chromic ion to chromous or alternatively to a change of ligands in the coordination sphere of the metal. A slow precipitation of a colorless solid was observed, but no evidence of formation of elemental chromium was found.

The $CrCl_3$-$NaBHCN(CH_3)_2$ System

In an attempt to counterbalance the electron withdrawing power of the cyano group, a borohydride ion was synthesized having in addition to the cyano group two electron supplying methyl groups. The reducing properties of the ion would reside in the single B-H bond which after reaction with chromium salts should leave a boron species, $(CH_3)_2BCN$, in which the boron would not tend to bond to chromium.

The unreported $NaBHCN(CH_3)_2$ was prepared in THF solution by treating $NaBH_2(CH_3)_2$ with a deficiency of HCN (Equation 20). On mixing the reducing

$$NaBH_2(CH_3)_2 + HCN \longrightarrow NaBHCN(CH_3)_2 + H_2 \qquad (20)$$

solution with $CrCl_3$, only a small quantity of hydrogen was formed (probably from the excess $BH_2(CH_3)_2^-$ ion), together with a gray solid. The resulting aqua colored solution precipitated chromium on treatment with $NaBH(CH_3)_3$, indicating that $NaBHCN(CH_3)_2$ had failed to reduce the chromium salt.

CONCLUSIONS

An immediate reduction of chromic chloride to chromous chloride occurs in tetrahydrofuran-diethyl ether solvent on treatment with lithium borohydride. A slower reaction, which can be accelerated either by addition of aluminum chloride or by decreasing the THF concentration, results in conversion of the chromous salt to a black X-ray amorphous solid of variable stoichiometry consisting primarily of chromium and boron in an approximately 1:2 mole ratio. It is presumed that intermediate chromous borohydride is unstable with respect to loss of hydrogen and/or borane groups, resulting in a "chromium boride" coating which becomes non-adherent in thicknesses over a few hundredths of a mil. An attempt to prevent co-deposition of boron with chromium by *in situ* formation of alkyl-substituted borohydride by reaction of an olefin with the borohydride ion was only partially successful in that considerably less boron was co-deposited. The weaker reducing agent, sodium cyanoborohydride, is capable of reducing chromic chloride to the chromous state. The resulting solution, which is stable toward further reduction, precipitates a colorless solid on standing.

Trialkyl- and dialkyl-substituted borohydride salts in tetrahydrofuran proved to be stronger reducing agents than borohydride itself. Both sodium triethyl- and the new trimethyl-borohydride are capable of near instantaneous reduction of chromic chloride to the metal as a colloidal-appearing black precipitate. The previously unknown sodium dimethylborohydride reduces chromic chloride to the chromous stage on mixing, followed in about a minute by precipitation of colloidal-appearing elemental chromium. The rapidity of reduction with these reagents, which resulted in precipitation in the bulk of the solution, precluded controlled plating on a metal

surface. A novel dimethylcyano-substituted borohydride salt, which by virtue of the alkyl groups should not co-deposit boron with the chromium, was too weak to effect reduction of chromic chloride beyond the chromous stage.

RECOMMENDATION

In view of (1) the rapidity of chromium deposition without plating when chromic chloride was reduced with alkyl-substituted borohydrides, (2) the formation of a non-adherent "chromium boride" plate when borohydride salts were used as the reducing agent, and (3) the inability of cyano-substituted borohydride to effect reduction to elemental chromium, further efforts to achieve a non-aqueous electroless chromium plating bath appear unwarranted at this time.

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